Micelle Studies of Dodecyltrimethylammonium Bromide in Water as Probed by Benzene: Effect on Shapes and Sizes of Micelles

Yoon Seob Lee and Kyu Whan Woo*

Department of Chemistry Education, Seoul National University, Seoul 151-742
Received April 9, 1993

Micellization process of dodecyltrimethylammonium bromide (DTAB) was studied by using the aromatic probe (benzene) which dissolved in aqueous DTAB solutions. Proton NMR chemical shift measurements of DTAB and DTAB-benzene system showed that benzene molecules solubilized near the micelle-water interface and that the solubilization sites within the micelles are different as the DTAB concentration is passing through 32.0 mM (hereafter we refer this concentration as the second CMC). The change of solubilization sites is also confirmed by abrupt changes of the chemical shifts and relaxation rates of benzene protons in DATB-benzene system at this concentration. It was revealed from the electrical conductivity and viscosity measurements that the solubilization of benzene caused the DTAB micelles to swell out and that the micelles prepared after the second CMC had a greater swelling effect than those prepared before the second CMC. The transition point which reflects the saturation of benzene molecules on the solubilization sites of micelles was observed at one benzene/micellized DTAB mole ratio from the electrical conductivity measurements. Along the different concentration of DTAB solution, this transition point is appeared clearly after the second CMC. From these results it is suggested that the shapes and/or sizes of DTAB micelles of the spherical micelle region prepared after the second CMC are different from those prepared before the second CMC.

Introduction

Micellization of cationic surfactants in aqueous media is known to proceed as (i) the formation of aqueous micelles through the cooperative association of surfactant monomer ions in a low surfactant concentration and (ii) the transition of aqueous micelles into the worm-like ones through the micelle growth in a high surfactant concentration in which the repulsive aqueous micelles themselves can have cooperative interactions each other.[1,2]

It is widely employed that the micelle shapes existing at aqueous micelle region are spherical or ellipsoidal including prolate and oblate.[3] Therefore this region is called the spherical micelle region. Stigter[4] has proposed that the aqueous micelle shapes of alkyltrimethylammonium bromide homologue series are transformed gradually from spherical to ellipsoidal as the carbon chain length is increased from 8 to 16. Lee[5] has reported that there is another critical concentration in spherical micelle region of aqueous alkylpyridinium chloride solutions of 12-16 carbon chain and argued that this may be occurred as a result of variation of micelle shapes. And Böhmer et al.'s[6] theoretical work defined these as a deformation of spherical micelles into ellipsoidal ones which can make the worm-like transition smooth.

Our recent NMR work[7] shows the existence of new critical micelle concentration (32.0 mM, refered as the second CMC) which differentiate the concentration range of the spherical micelle region into two sections in aqueous DTAB solutions. The extent of penetration of water molecules and the content of penetrated water molecules near the micelle-water interface are attributed to the main factor of this existence. In this study we try to obtain another proof by using the probe which controls the penetrated water molecules near the micelle-water interface. Many optical probes are used in studies of the properties of micelles including water penetration, swelling effect of micelles by additives, quenching effect by

micelles, etc.[8] A common feature of all probes used is that they contain aromatic ring and/or polar functional groups.

We select benzene for this purpose because (i) it is mildly surface-active and solubilizes at the micelle-water interface near the head groups in ionic-micelles and (ii) benzene should perturb the micelle structure much less than the other probes.[8a]

Experimental

DTAB having 99.9% purity was purchased from Aldrich-Chemie, West-Germany and used as supplied without further purification. It was dried *in vacuum* at room temperature for at least 3 days before use. Deuterium oxide was supplied by Sigma Chemical Co. USA and was 99.9% enrichment. Water having electrical conductivity below 3 μS/cm was used. Benzene (Junsei Chemical Co., Extra pure) was purified by shaking with conc-H_2SO_4 until free from thiophen, then with water, dil-NaOH and water, followed by drying with $CaCl_2$, and distilled after being refluxed with Na for 3 days.

Proton NMR chemical shift measurements were made on a Bruker AMX-500 NMR spectrometer operating at 11.75 T (tesla) magnet at Korea Basic Science Center (Seoul) and proton spin-lattice relaxation rates were measured on a Hitachi R-600 high resolution NMR spectrometer operating at 1.41 T magnet. The deutrium signal from D_2O was employed as an internal lock. Probe temperature was calibrated from the chemical shift difference between the two proton resonances of standard methanol sample.[9] The oxygen was removed by freeze-pump-thaw cycles repeated at least 5 times, and the NMR tubes were sealed under vacuum condition. All resonance line positions of DATB and benzene hydrogens were measured relative to the residual HOD proton resonance ($\delta = 4.800$ ppm) as an internal reference. Relaxation rates were measured by the conventional inversion-recovery method. Reported chemical shifts and relaxation rates are
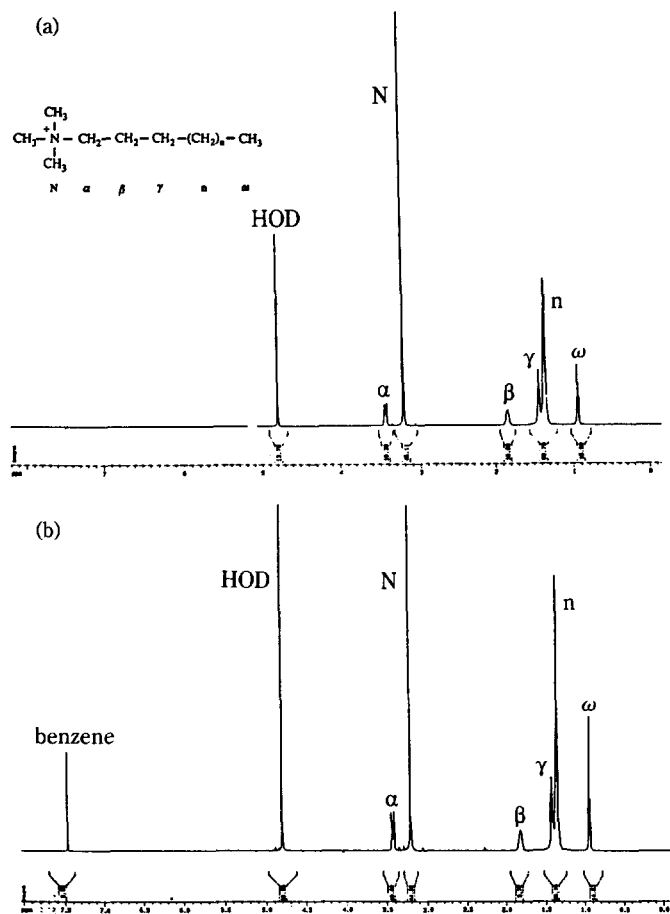
Figure 1. Proton NMR spectra of (a) 0.045 M aqueous DTAB solution and (b) 0.045 M aqueous DTAB-benzene (0.67 benzene/micellized DTAB mole ratio) solution obtained at 11.75 T magnet. Spectra of DTAB and DTAB-benzene at other surfactant concentrations studied also do not show any benzene-induced multiplicity for the existing proton signals and only show the chemical shift changes. Assigned proton signals of DTAB molecules are inserted in part (a).

Figure 2. Benzene-induced NMR chemical shift changes, $\Delta\delta$, of various protons of DTAB molecules in each surfactant concentrationl. $\Delta\delta = |\delta$ of DTAB protons$|$-$|\delta$ of DTAB-benene (0.67 benzene/micellized DTAB mole ratio) protons$|$. Positive $\Delta\delta$ values mean up-field shift and negative ones mean down-field shift.
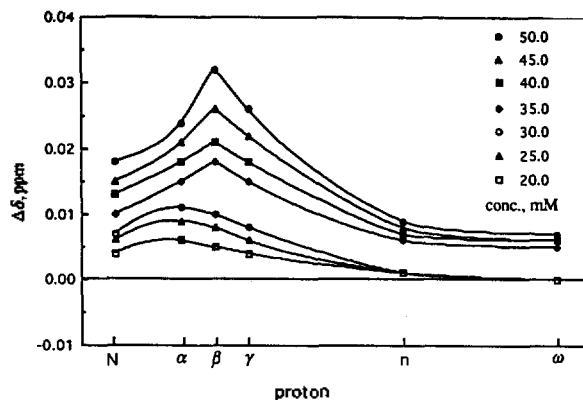
average values of 3~5 separate measurements.

Electrical conductivity measurements were made using a TOA Model CM-30ET conductivity meter, while viscosity of the solutions was measured with a Witeg UBB 5408 Ubbelohde viscometer. Every reported value is a mean of 7~10 seperate readings.

All experiments for the study were performed at $34.2°C$.

Results and Discussion

It is safe to work with a probe as low content as possible in order to minimize any perturbations in the micelle structure. Thus in order to find optimum condition in NMR experiment of obtaining chemical shifts change of DATB protons and of intensity of benzene proton itself, we made the benzene/micellized DTAB mole ratio as 0.67. We know that the first CMC of DTAB in water is 15.0 mM.[1] Below the first CMC in DTAB solution saturated with benzene only trace amounts of benzene is detected by UV spectrometry, we thus neglect the amounts of benzene existing in aqueous phase of DTAB solution. Above the first CMC benzene is easily

solubilized about twice of micellized DTAB concentration. Therefore we regard that benzene is located near and in the micelle parts including Stern and Gouy-Chapmann layer.

The results obtained from the measurements of diffusion coefficient and electrical conductivity[10] show that the aggregation number of DTAB micelle has little variation by the addition of benzene except that the micelle is deformed at higher benzene content *i.e.*, above one benzene/micellized DTAB mole ratio. Thus we assume that the structure of DTAB micelle has little disturbance by the addition of benzene up to about one benzene/micellized DTAB mole ratio and consider that the primary effect of benzene dissolving in aqueous DTAB solution is to increase the size of the micelles. As benzene is solubilized it seems reasonable that the micelles will be swollen and increase in size.

In every concentration studied, the addition of benzene does not change the line shape of DTAB protons (Figure 1) and only changes the amount of chemical shift variously (Figure 2). This would suggest that the life time of benzene is faster than the NMR chemical shift time scale and that the various surfactant segments exhibit the differential exposure to the ring-current effect of the benzene ring. The sign and magnitude of the ring-current shift is highy dependent upon the orientation of the benzene ring. Protons above/below the benzene ring experience enhanced shielding due to the negative contribution of the ring to the local magnetic field (up-field shift) and protons that are in the plane of the ring do a decreased shielding. In our NMR works all segments of DTAB molecules experience a up-field shift in DTAB-benzene system and the maximum shifts are observed around the first three methylene units of dodecyl-chain in every concentration from 20 to 50 mM studied (Figure 2). Along the above concentration range, in the first section (20-30 mM) of the spherical DTAB micelle region the maxima are observed around the head group near the micelle interior and n and ω segments do not show a detectable shift. However in the second section (35-50 mM), the maxima are shifted to the deeper parts of the micelles and n and ω segments also experience considerable up-field shift. Moreover benzene protons also show up-field shift as well as increased spin-lattice relaxation rate as DTAB concentration is in-
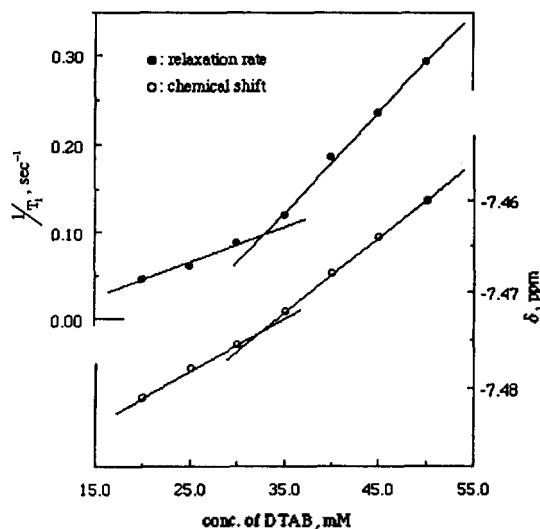
Figure 3. Plot of proton spin-lattice relaxation rates and chemical shifts of benzene protons in DTAB-benzene (0.67 benzene /micellized DTAB mole ratio) system as a function of the surfactant concentration.

creased and have abrupt changes around the 32.0 mM (the second CMC) in both of these NMR parameters (Figure 3). This indicates the more restriction of motions of benzene molecules in the micelles of the second section. We consider from these observations that the solubilization processes of benzene molecules in DTAB micelles are differentiated around the 32.0 mM spot, and those can be attributed to the difference in shape and/or size of DTAB micelles in each section.

The electrical conductivity, κ, of ionic surfactant systems has been shown to be[11]

$$\kappa = \frac{e^2}{k_B \cdot T} \cdot \left(\sum Z_i^2 \cdot D_i \cdot C_i + Z_m^2 \cdot D_m \cdot C_m \right)$$

where e is the fundamental unit of charge, k_B is Boltzmann's constant. Z_i, Z_m denote the valences, C_i, C_m denote the concentrations and D_i, D_m denote the diffusion coefficients of ionic species i or micelle species m respectively.

In case of aqueous DTAB-benzene systems, our electrical conductivity measurements show that $\Sigma Z_i^2 \cdot D_i$ is constant. And the degree of the counterion ionization of DTAB (0.27) is obtained from the slope ratio between monomer and micelle region of the plot of electrical conductivity against total DTAB concentration. Therefore Z_m is determined as constant of $0.27 \cdot n$ (where n is aggregation number). Since we have confirmed that the first CMC does not vary in various amounts of added benzene from electrical conductivity measurements, it is evident that the electrical conductivity, κ, is proportional to the diffusion coefficient of DTAB micelles, D_m. Therefore the decreasing of electrical conductivity as benzene content is increased in Figure 4 reflect the swelling of DTAB micelle by benzene. Around a benzene content approximately one benzene/micellized DTAB mole ratio, there is a tendency of changing in slope of the electrical conductivity curve in every DTAB concentration. This can be interpreted partly due to stoichiometic saturation of benzene with DTAB micelle and partly due to change of solubilization pro-
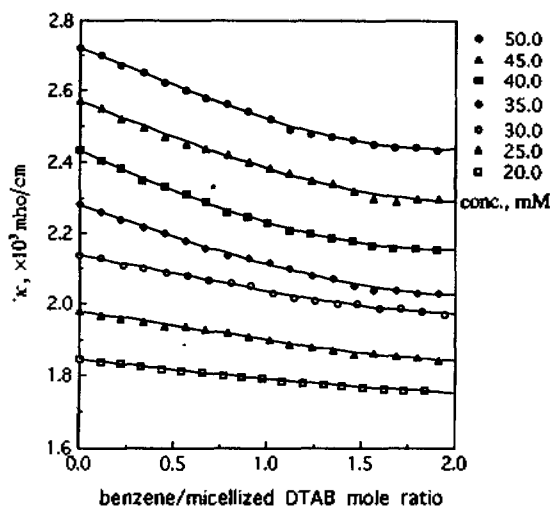

Figure 4. Effect of benzene on electrical conductivity of aqueous DTAB solutions at each surfactant concentration.
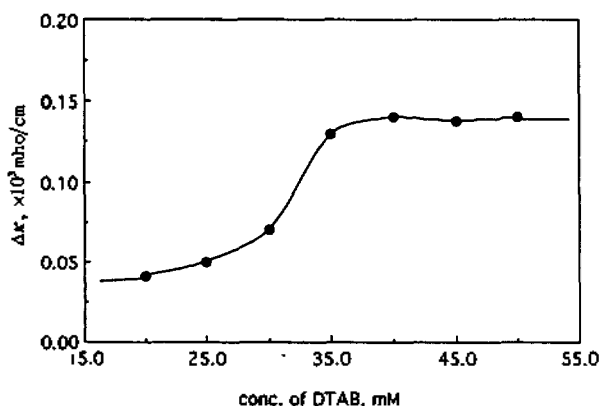
Figure 5. Benzene-induced changes in electrical conductivity of aqueous DTAB solutions, Δκ, above the first CMC. Δκ = {electrical conductivity of DTAB solution } -{electrical conductivity of DTAB-benzene (0.67 benzene/micellized DTAB mole ratio) solution}.

cess, i.e., dissolving of benzene up to the central parts of the micelle, which can be related to the possibility of the benzene perturbing the structure of the micelles. But in two sections of the spherical micelle region, marked differences were observed before and after this saturation point. Decreasing of electrical conductivity i.e., swelling of micelle by benzene, is more pronounced at the second section (35-50 mM) and also the saturation point is more obvious. It is evident from these and NMR chemical shifts results that the shapes of DTAB micelles in two sections of spherical micelle regions are different, and the micelles in the second region are probably nonspherical since the dissolving of benzene to the direction of the central parts of the micelles may be more pronounced as the micelles become less spherical and more rodlike. And this is confirmed more practically in results of electrical conductivity and viscosity measurement at 0.67 benzene/micellized DTAB mole ratio. The difference in electrical conductivity between DTAB solution and 0.67 mole ratio DTAB-benzene solution, Δκ, is large at the second section (Figure 5).
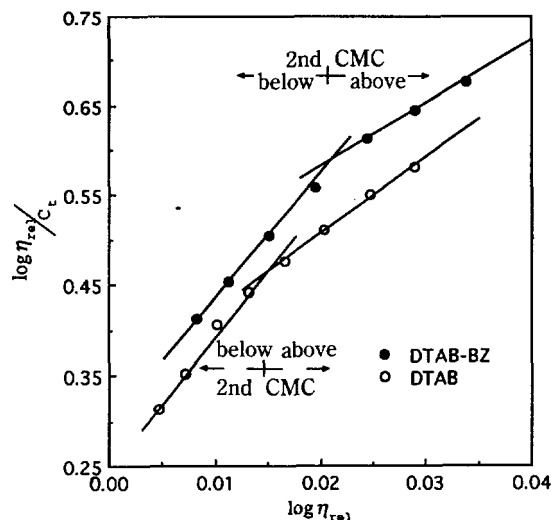
Figure 6. Plot of $\log\eta_{rel}/c_t$ versus $\log\eta_{rel}$ of aqueous DTAB and DTAB-benzene (BZ) (0.67 benzene/micellized DTAB mole ratio) solutions above the first CMC.

Table 1. Molar Volumes[a] of Spherical Micelles in Aqueous DTAB and DTAB-Benzene (BZ) (0.67 benzene/micellized DTAB mole ratio) Solutions

System \ Region	Before the 2nd. CMC	After the 2nd. CMC	Ratio
DTAB	0.235	0.320	1.36
DTAB-BZ	0.279	0.400	1.43
Ratio	1.19	1.25	

[a]Unit: litre/mole.

Ekwall and Holmberg[12] found that the variation of the viscosity of ionic surfactant solutions which is valid for spherical micelles can be represented as

$$\log\eta_{rel}/c_t = A_3 + Q' \cdot \log\eta_{rel}$$

$$A_3 = 2.5 \cdot \overline{V}/2.303, \qquad Q' = Q \cdot \overline{V}$$

where C_t is the total surfactant concentration. In this equation $\overline{V}$ (litre/mole) is the molar volume of the micelle including the hydrated water molecules and Q is an interaction parameter. We obtain the constant values of A_3 at the first section (20-30 mM) of DTAB micelles and obtain some larger ones at the second section in both DTAB and DTAB-benzene system (Figure 6). The calculated molar volumes are listed in Table 1.

Now the above statements can be identified quantitatively with the results of micelle molar volumes of DTAB and DTAB-benzene systems in each micelle sections. Larger ratio

of molar volume between each micelle section in DTAB-benzene system in comparison with the one in DTAB system is arised from the greater swelling effect of benzene in the second section. This is also related to the different solubilization process of benzene in each of the two micelle section and suggest that solubilization of benzene to inner part of the micelle results in a greater micelle size increase than solubilization near the micelle-water interface.

The phenomenon of solubilizaion of benzene in aqueous DTAB solution by interaction with micelles can be understood on the viewpoint of thermodynamic approach. In aqueous micellar solution, some water molecules penetrate into the hydrocarbon parts of the micelles to some extent. It is certainly favorable that benzene is substituted for this penetrating water molecules because of the high polarizability of the benzene ring. Thus in the DTAB-benzene system evenly solubilized benzene molecules around Stern-layer may lower its energy in comparison with the case that benzene molecules are penetrated within the micelle interior deeply.

References

1. J. H. Fendler, "Membrane Mimetic Chemistry", Wiley, New York (1982).
2. J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular Systems", Acadedic Press, New York (1975).
3. C. Tanford, "The Hydrophobic Effect: Formation of Micelles and Biological Membranes", 2nd. Ed., Wiley, New York (1980).
4. D. Stigter, *J. Colloid Interface Sci.*, **23**, 379 (1967).
5. M. I. Chung, I. J. Tak, and K. M. Lee, *DAEHAN HWA-HAK HWOEJEE*, **19**, 398 (1975).
6. M. R. Böhmer, L, K. Koopal, and J. Lyklema, *J. Phys. Chem.*, **95**, 9569 (1991).
7. Y. S. Lee and K. W. Woo, *Bull. Korean Chem. Soc.*, **14**, 392 (1993).
8. (a) J. C. Eriksson and G. Gillberg, *Acta Chem. Scand.* **20**, 2019 (1966); (b) F. M. Menger, J. M. Jerkunica, and J. C. Johnston, *J. Amer. Chen Soc.*, **100**, 4676 (1978); (c) R. L. Reeves, R. S. Kaiser, and H. W. Marks, *J. Colloid Interface Sci.*, **45**, 396 (1973); (d) C. A. Bunton, A. Kamego, and M. J. Minch, *J. Org. Chem.*, **37**, 1388 (1972).
9. M. L. Martin, G. J. Martin, and J. J. Delpuech, "Practical NMR Spectroscopy", Heyden, London (1980).
10. K. Kandori, R. J. McGreevy, and R. S. Schechter, *J. Phys. Chem.*, **93**, 1506 (1989).
11. A. C. Lam, Ph. D. Dissertation, The University of Texas, Austin, TX, (1986).
12. P. Ekwall and P. Holmberg, *Acta Chem. Scand.*, **19**, 573 (1965).